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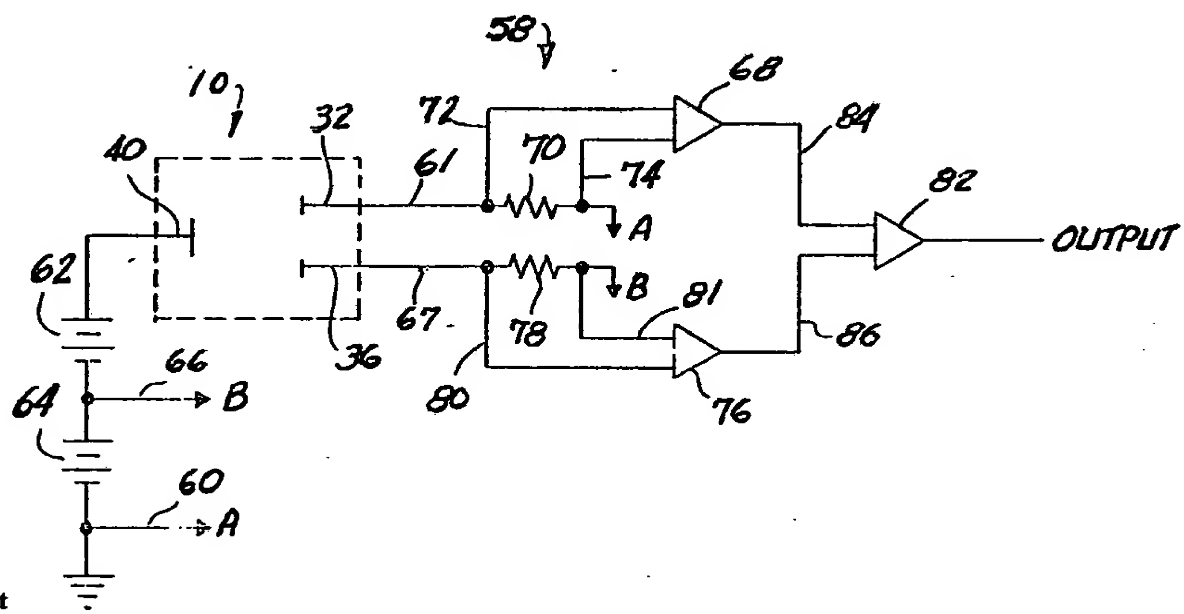


(57) Abstract

Method and apparatus are disclosed for the electrochemical determination of an electrochemical reactive substance in a fluid stream and for simultaneously determining and subtracting from the current flow due to the reaction of the sought for substance, current flow caused by non-Faradaic conditions and other non sought for electrochemically reactive substances. The sensor consists of a counter electrode (40), a sensing electrode (32) and a compensating electrode (36). The sensing electrode is biased to the concentration polarization potential of the sought after substance while the compensating electrode is biased to a different potential sufficiently low to cause current flow between the counter electrode and the compensating electrode due to non-Faradaic phenomena and/or other electrochemically reactive substances which react below the potential of the sensing electrode. Circuitry is provided for subtracting the compensating electrode signal output

NOISE REDUCTION TECHNIQUE FOR ELECTROCHEMICAL CELLS

Field of Invention

The present invention relates to a method and apparatus for the electrochemical determination of a gas or gases in a fluid and more particularly to a method and apparatus for the simultaneous correction for background current and for the determination of more than one gas by a single electrochemical sensor assembly.

Background of the Invention

The measurement of the partial pressures of electrochemically reactive substances, such as dissolved gases in fluids, by the measurement of current produced by the electrochemical reaction of the test gas at an electrode is well known in the art. Pursuant to this technique, the current flow between a working electrode and a counter electrode due to the electrochemical reaction of the gas is proportional to the partial pressure of the gas and provides a direct readout of the gas partial pressure. Widely used for this technique are amperometric electrochemical cells which contain a suitable electrolyte and which are provided with an opening adjacent the working electrode which is sealed with a membrane permeable to the sought for substance. Such devices, which may operate galvanically or with an external polarization voltage source, are utilized, for example, for the detection of oxygen, CO_2, NO, NO_2 and the like. Determination of such substances is highly critical in the control of industrial processes where these substances may be considered as contaminants in a fluid stream. Likewise, the detection of such substances by electrochemical determination is highly useful in

biochemical analysis, particularly the detection of O_2 and CO_2 in body fluids. Moreover, even if only a single substance is to be determined, the presence of other substances which are electrochemically active at the polarization voltage level of the working electrode can be considered as interfering substances which contribute to the background noise and which may produce erroneous results or cause loss of instrument sensitivity unless current flow due to electrochemical reaction of such substances is detected and compensated.

Substances, such as dissolved gases, are electrochemically detected by imposing a potential between a working electrode and a counter electrode which is such that the particular gas being sought undergoes an electrochemical reaction to produce a current flow between the counter electrode and the sensing electrode which is proportional to the partial pressure of the gas being sought. Normally a sensor is able to detect only a single gas although electrochemical detectors are available in the art for the simultaneous measurement of two gases, such as, for example, O_2 and CO_2, U.S. Patent 4,452,672 (Parker et al.). The Parker et al. sensor operates by biasing the potential at the working electrode to the concentration polarization potential (full wave potential) at which O_2 undergoes electrochemical reduction and simultaneously measuring current flow at the half wave potential of CO_2. Such a sensor, however, requires circuitry for determining the slope of the current/potential curve and for differentiating the current measured at the half wave potential of one of the gases being determined from current measured at the full wave potential of the other gas being determined. In addition, sensors of this type are actually determining the second gas by measuring the change in

current due to changes in the pH of the electrolyte caused by the presence of the second gas. However, pH shift may also be due to other factors which are independent of the presence of the second gas such as for example, the presence of other unsought for gases, which will influence the current shift and may adversely affect the current flow.

Other types of sensors for the measurement of more than one gas have been proposed. Such devices normally include a glass pH electrode and such sensors are not suited for use in industrial applications where severe operating conditions such as high temperature and the like may be encountered.

A closely related problem encountered with electrochemical sensors is the necessity of recalibrating the sensor due to changing operating parameters which affect current flow. Such parameters include temperature and residual current flows due to other phenomena not related to the electrochemical reaction of interest. For example, residual currents may be caused by phenomena not related to the Faradaic electrochemical reaction being measured, such as double layer capacitance charging currents and transient currents coupled into the amplifier through the sensor. These residual currents are referred to herein as non-Faradaic current. In addition, background currents which affect the current measurement of the electrochemical reaction are often caused by interferant substances contained in the electrolyte or which enter the electrolyte and which, at the sensing electrode potential, may enter into a cross-competing electrochemical reaction with the resultant production of a signal which is not related to the sought for gas. Unless compensated for in the sensor or unless the sensor is recalibrated, such signals will erroneously affect the output measurements.

<u>Summary of the Invention</u>

The present invention provides a method and apparatus for the electrochemical detection of one or more electrochemically reactive substances in a fluid and for the compensation for background current without the necessity of continuous or constant recalibration. As used herein the term substance refers to any electrochemically reactive material in a test fluid but the invention will be described hereinafter primarily in connection with any electrochemically reactive gas dissolved in a test fluid. The sensor provided herein is inexpensive to manufacture and since it does not involve the use of glass electrodes or reference electrodes, the sensor is highly suited for use in industrial applications where severe operating conditions may be encountered. By the same token, the sensor is highly sensitive and is suited for use in biochemical applications, such as for example the measurement of oxygen and CO_2 in blood.

The apparatus of the present invention comprises a body defining a reservoir for electrolyte. A sensing electrode and a counter electrode are disposed in the reservoir of the sensor body. The sensing electrode has a working surface located adjacent the permeable wall portion of the body and the counter electrode is disposed in the reservoir and is connected for current flow to the sensing electrode through the electrolyte. In accordance with the invention, the sensor further includes at least one compensating electrode which is located in the sensor body adjacent the sensing electrode. The compensating electrode includes a working surface which, for the purpose described hereinafter, can be disposed inwardly in the reservoir with respect to the working surface of the sensing electrode or in the same plane as the working surface

of the sensing electrode. In either case, however, the compensating electrode is proximate to the sensing electrode. The compensating electrode is also electrically connected to the counter electrode through the electrolyte. Circuit means are provided for imposing a potential between the working electrode and the counter electrode and a different potential between the compensating electrode and the counter electrode. Means are provided for measuring current flow between the counter electrode and the sensing electrode and between the counter electrode and the compensating electrodes. Comparitor means are provided for determining an incremental component of the current flows being measured. The sensing electrode and each of the compensating electrodes are biased at different potentials so that the component of current flow between a compensating electrode and the counter electrode due to interfering substances can be subtracted from the total current flow as measured between the sensing electrode and the counter electrode to arrive at the component of current flow due solely to the sought after substance. As used herein the term "working surface" is used to designate the effective area of an electrode at which an electrochemical reaction takes place.

In accordance with the method of the present invention the sensing electrode is biased to a potential to cause the electrochemical reaction of the sought after gas at the working surface of the sensing electrode and the compensating electrode is biased to a potential which is usually lower but in no event greater than that of the sensing electrode, to produce current flow due to the electrochemical reaction of interferant gases at the working surface of the compensating electrode and to include any non-Faradaic current flow. The current flow between the sensing

electrode and the counter electrode is the total current flow through the cell and is the aggregate of current flows at the potential of the sensing electrode due to all causes. The current flow between the counter electrode and the compensating electrode is subtracted from this total current flow. The difference thus arrived at is the diffusion current flow between the counter electrode and the sensing electrode due solely to the electrochemical reaction of the sought after gas which is directly proportional to the partial pressure of the sought after gas in accordance with Faraday's law.

By the application of this subtractive technique to the measurement of current flow in the cell, the necessity of frequent recalibration of the cell is eliminated since changes in current flow due to changing conditions in the electrolyte will be automatically subtracted out of the output reading. In addition, however, one may take advantage of the electrochemical reactivity of a different gas or gases ,which are normally considered as interfering gases, to measure the partial pressure thereof. A single set of electrodes may be utilized and means provided for changing the potential between the sensing electrode and the counter electrode to correspond to the concentration polarization potential of the sought for substance, and for setting the compensating electrode potential below that of the sensing electrode but high enough to include residual current flow due to non-Faradaic causes and/or the concentration polarization potential of any interferant substances which are below that of the sought after gas. The current flow between the compensating electrode and the count

electrochemical reaction of the sought for gas. The potential of the sensing electrode is then increased to the polarization concentration potential of the next gas to be determined and the potential of the compensating electrode is likewise increased to at least the level at which the sensing electrode was previously biased so as to compensate for the diffusion current flow of the previously determined gas plus any other current components due residual current, and the determinations repeated in the manner described. This may be carried out for any number of gases which have concentration polarization potentials below the decomposition potential of the electrolyte. Likewise, however, the sensor may be constructed in accordance with the present invention with a plurality of electrodes which are biased at different potentials and which may serve both as compensating electrodes and as sensing electrodes.

The term "concentration polarization potential" as used herein means that potential where only as much current can flow as is determined by the rate of diffusion of an electrochemically reactive substance to the electrode surface where it undergoes immediate reaction. This current flow less any residual or background current is referred to as the "diffusion current".

In yet another aspect of the invention, the compensating electrode may serve as a scavenger for the elimination of an undesired interferant substance before it reacts at the sensing electrode and effects the current flow to the counter electrode. This is accomplished in accordance with the invention by having a compensating electrode biased to a different potential than the sensing electrode but at a potential which is within the range of concentration polarization potential of the interferant substances. Preferably in

potential of the interferant substances. Preferably in this mode an effective area of the compensating electrode is located in the sensor reservoir adjacent the sensing electrode but spaced inwardly in the sensor from the sensing electrode. It should be noted that the interferant substance may be the same species as the sought after gas. For example, one application of particular interest is the elimination of the effect of dissolved oxygen in the bulk electrolyte where the compensating electrode acts to reduce the dissolved oxygen in the area adjacent the sensing electrode so that the startup period is substantially reduced and the sensor quickly comes to zero after startup and changes in current flow during the operation of the sensor, due to such dissolved oxygen are immediately compensated.

Brief Description of the Drawings

The invention will be more fully illustrated and explained in the following detailed description of the invention taking in conjunction with the accompanying drawings in which:

FIG. 1 is a side elevation, partially in section, of an electrochemical sensor constructed in accordance with the present invention;

FIG. 2 is a sectional view in enlarged scale and partially broken away for compactness of illustration of an electrode assembly for use in the electrochemical sensor of FIG.1;

FIG. 3 is a view of the sensor of FIG. 2 taken along line 3-3;

FIG. 4 is a schematic diagram of circuitry for imposing different potentials on the sensing electrode and the compensating electrode and for subtracting the compensating electrode current from the sensing electrode current to determine the incremental

component of current flow due to the sought after substance;

FIG. 5 is a schematic polarogram for oxygen;

FIG. 6 is a schematic polarogram for five substances dissolved in a test fluid for which a determination may be made; and

FIG. 7 is a schematic diagram of circuitry for the embodiment of the sensor of the invention employing a plurality of electrodes which serve both as esnsing and compensating electrodes.

Detailed Description of the Invention

Referring to FIG.1, there is illustrated an electrochemical sensor, generally designated as 10, comprising a cylindrical body 12 having a recess 14 defining an electrolyte reservoir extending substantially through the body 12 and further defining an opening 16 at one end thereof. A second opening 18 is provided in the wall of the body 12 and is closed by a plug 20 which is screw threaded into the second opening 18 and which is used for the introduction of electrolyte. The recess 14 is closed by means of a membrane 22 which is stretched across the opening 16 of the recess 14 and held there by a retainer 24 which is clamped between the end of the body 12 and a cap 26 which is threadably engaged with the end of the body 12. The membrane, which serves as a permeable wall to close the opening 16 in the body 12, is selected from a material that is permeable to the sought for substance or substances and impermeable to the electrolyte. Suitable membrane materials are well known in the art and include polyethylene or polytetrafluorethylene. The cap is provided with a central opening 28 for contact between the membrane 22 and a test fluid.

The body 12 further includes a central member 30 which is disposed in the recess 14 and which supports a

sensing electrode 32 having a working surface 34 which is disposed adjacent the membrane. In the embodiment illustrated in FIG. 1, a compensating electrode 36 which is in the form of a disk 36a having a central aperture 36b, an upper face 36c and lower face 36d, is concentrically disposed about the sensing electrode 32 and the compensating electrode 36 is suitably affixed to the supporting member 30, such as by bonding to the central member 30 with a suitable adhesive. The upper face 36c defines a working surface of the compensating electrode 36 proximate to but disposed inwardly in the reservoir with respect to the working surface 34 of the sensing electrode 32 to serve as a scavenger electrode as will be described. The lower face 36d of the electrode preferably lies in the same plane as the working surface 34 of the sensing electrode 32 for the most accurate determination of current flow due to residual current and/or interferent substances. A counter electrode 40 is disposed interiorly of the sensing electrode 32. Each of the electrodes 32, 36 and 40 are connected to a terminal 44 by a lead 46, 48, and 50 respectively. The terminal 44 includes appropriate electrical connections 52 , 54, and 56 for connecting the cell to external circuitry 58.

When the sensor is used for the polarographic measurement of oxygen, the sensing electrode 32 and the compensating electrode 36 may be formed of gold or other noble metal and may be the same or different materials and the effective area of the compensating electrode 36, that is the total surface area exposed to electrolyte and to electrochemical reactive materials, may be the same as or greater than the effective area of the sensing electrode 32. In the embodiment illustrated, the effective area of the sensing electrode 32 is equivalent to the working surface 34 thereof.

The electrolyte utilized in the sensor of the present invention may be any of the commonly employed electrolytes such as aqueous solutions of potassium hydroxide (2%) or if severe conditions with respect to temperature are to be encountered, more sophisticated electrolytes such as organic supporting electrolytes. Such organic supporting electrolytes may be selected from temperature resistant materials such as for example, the amino alcohols, morpholine or the like which contain supporting electrolytes such as potassium chloride to provide electrical conductivity. Such temperature resistant electrolytes are disclosed in United States Patent 4,268,370 and do not per se form a part of the present invention. The electrolyte may be buffered to reduce the effect of contaminant substances which change the pH of the electrolyte.

As illustrated in FIG. 4, the schematic diagram of the circuitry 58 for the sensor illustrated in FIG. 1 includes the sensor in which is disposed the sensing electrode 32, compensating electrode 36 and the counter electrode 40. The sensing electrode 32 is biased to a potential with respect to the counter electrode 40 through a circuit consisting of a line 60, and power supply 62 and 64 and a line 61. The circuit between the sensing electrode 32 and the counter electrode 40 is completed through the electrolyte in the sensor. Similarly the compensating electrode 36 is biased to a potential with respect to the counter electrode 40 through a line 66, the power supply 64 and a line 67. An amplifier 68 is connected on either side of a resistor 70 in the line 60 through lines 72 and 74 and a corresponding amplifier 76 is likewise connected on either side of a resistor 78 in the line 66 by lines 80 and 81. The output of the amplifier 68 and the amplifier 76 is directed to an operational amplifier 82 through lines 84 and 86 respectively. The operational

amplifier 82 serves to subtract any current flow between the compensating electrode 36 and the counter electrode 40 from the total current flow between the sensor electrode and the counter electrode 40 and the output is the component of current due solely to the diffusion current produced by electrochemical reactions at the sensing electrode 32 at the concentration polarization potential at which it is set.

The operation of the sensor will be described in connection with the embodiment illustrated in FIG. 1 for the determination of oxygen. However, it will be understood that in accordance with an embodiment of the present invention and the discussion relating thereto, the concentration polarization potential of the sensing electrode 32 can be readily varied for the determination of other electrochemically reactive substances such as NO, NO_2, and Cl_2.

The reservoir of the body 12 is filled with a suitable electrolyte for oxygen determination, preferably a 2% aqueous solution of potassium hydroxide through the second opening 18 in the body 12 and sealed by the plug 20. The sensing electrode 32 is biased to a potential of -750 millivolts and the compensating electrode 36 is biased to a potential of about -200 millivolts. In the embodiment illustrated herein, the compensating electrode 36 is set at a potential well away from the concentration polarization potential of oxygen to detect non-Faradaic residual current flow.

The selection of the potentials for the sensing electrode 32 and the compensating electrode 36 are best illustrated in FIG. 5 which is a polarogram for oxygen. As illustrated, there is a relatively minor change in current between 0 and about -200 millivolts (B) at which point there is a sharp increase in current to the plateau of the curve (C and D). The current flow

which occurs between the points A and B of the curve is referred to as residual current or background current. The area of the curve between points B and C is referred to as the depolarization region in which there is an increasing current flow with relatively small change in potential and the area on the plateau of the curve between points C and D is referred to as the concentration polarization region or the diffusion limiting plateau. It is at this point that the flow of current is the diffusion current that is directly proportional to the electrochemical reaction of the sought for substance at the electrode and is relatively independent of applied potential. The potential range through the concentration polarization region is referred to as the concentration polarization potential and preferably the sensing electrode 32 is biased to a potential in the middle of this region, which for oxygen is normally -750 millivolts. It will be apparent, however, that higher or lower potentials can be selected and still be in the range of concentration polarization potentials for oxygen.

A test fluid is introduced to the membrane 22 of the sensor through the opening 16 and any oxygen present in the test fluid will permeate the oxygen permeable membrane 22 and contact the working surface 34 of the sensing electrode 32 where it is electrochemically reduced with a resultant diffusion current flow between the sensing electrode 32 and the counter electrode 40. The compensating electrode 36 which is biased at a lower potential will not electrochemically reduce oxygen but will convey the background or residual current. Residual current is also a component of the current flow between the sensing electrode 32 and the counter electrode 40 in addition to the diffusion current.

Current passes from the sensing electrode 32

through the line 60 and the line 72 to the amplifier 68. Similarly, the residual current flows through the line 66 to the amplifier 76. The output of the amplifier 68 is the sum of current flow produced by residual current and by the electrolytic reduction of oxygen and is conveyed to the operational amplifier 82 through the line 84. The output of the amplifier 76, is the current flow due to residual current only and it also is passed to the operational amplifier 82 by the line 86. The operational amplifier 82 subtracts the output of the amplifier 76 from the output of the amplifier 68 and the signal output of the operational amplifier 82 represents the diffusion current flow due to the electrochemical reduction of oxygen and is conducted to means (not shown) to determine the partial pressure of oxygen contained in the test fluid.

As mentioned, other gases such as for example, Cl_2, NO_2, CO_2 and NO, may also be present in the test fluid. These gases are capable of electrolytic reduction if the sensing electrode 32 is biased to a potential equal to or in excess of the concentration polarization potential for such gas or gases. The electrolytic reduction of the gases will produce current flow which may result in erroneous results if not compensated for.

Referring to FIG. 6, a polarogram is illustrated showing current flow vs. potential for the above mentioned gases. Each of the gases has a characteristic nominal concentration polarization potential as compared to a normal hydrogen electrode as follows:

Cl_2 ____	+900 mV vs NHE
NO_2 ____	0 mV vs NHE
O_2 ____	-750 mV vs NHE
CO_2 ____	-600 mV vs NHE
NO ____	-1400 mV vs NHE

Thus, for oxygen determination, the compensating

electrode 36 should be biased to 0 mV, the concentration potential of NO_2, to determine the components of current flow due to residual current and the electrochemical reduction of Cl_2 and NO_2. These current flow components are subtracted in the manner already described from the total current flow between the counter electrode 40 and the sensing electrode 32 so that the output from the operational amplifier 82 represents the diffusion current due to the reduction of oxygen.

It will be evident from the foregoing discussion that the polarization bias of the sensing electrode 32 and the compensating electrode 36 can be adjusted so as to determine a plurality of different gases in a test fluid. Thus, for example, in the example illustrated in FIG. 6, a series of determinations can be made first with the sensing electrode 32 biased to the concentration polarization value of Cl_2 and the compensating electrode 36 biased to the background or residual current potential. A second reading is then taken with the potential of the sensing electrode 32 equal to the concentration polarization potential of NO_2 and the potential of the compensating electrode 36 equal to the concentration polarization potential of Cl_2. In this format the output of the sensing electrode 32 is the total of current flow components due to the reduction of NO_2, Cl_2 and the residual current while the output of the compensating electrode 36 is equal to the sum of current flow due to the reduction of Cl_2 and the residual current. By subtracting the current outputs of the compensating electrode 36 from that of the sensing electrode 32 in the manner described above, the output from the operational amplifier 82 is the diffusion current flow due to the reduction of NO_2. This process is repeated through the entire range of concentration polarization

potentials for the gases desired to be determined.

The potential of the sensing electrode 32 and the compensating electrode 36 may be readily varied by any conventional method such as by a variable resistance device of conventional design. In this case the sensor need only contain a single sensing electrode 32 and a single compensating electrode 36 and the various gases are determined sequentially. However, as shown in FIG. 2 and 3, the sensor may include several electrodes which can serve simultaneously as compensating electrodes and sensing electrodes.

Referring now to FIG. 2 and 3, the supporting member 30 is illustrated as carrying four electrodes which serve both as sensing electrodes 32 and as compensating electrodes 36. In this embodiment the working surfaces of each of the electrodes lie in essentially the same plane adjacent the membrane 22 and the concentric compensating electrode 36 illustrated in FIG. 1 may be eliminated if there is no desire for a guard electrode to cause an electrochemical reaction of electrochemically reactive interferant substances in the bulk electrolyte. The membrane 22 must be permeable to the series of gases to be determined. Such membrane compositions are well known in the art and do not form a part of this invention.

The circuitry 58 of FIG. 4 is modified to include additional amplifiers for the additional electrodes and means are provided for simultaneously subtracting current flows from electrodes of lower potential from the current flow of the electrode biased at the desired concentration polarization potential of the particular gas being tested for. Such a circuit is illustrated in FIG. 7, where the sensor 10 includes four sensing and compensating electrodes 88, 90, 92 and 94 which are biased to successively higher potentials with respect to a counter electrode 96 through a line 98 and series

connected power supplies 100, 102, 104 and 106. Each of the electrodes 88, 90, 92 and 94 are connected to an amplifier 108, 110, 112, 114 and 116 respectively in the manner described for the circuitry shown in FIG. 3. The output of the amplifier 114 and 112 is directed to an operational amplifier 118 where the output of the amplifier 114, which represents essentially non-Faradaic residual current, is subtracted from the output of amplifier 112. Thus, the output of the operational amplifier represents the diffusion current flow at the potential at which the electrode 92 is biased. At the same time, output from the operational amplifier 118, which represents the aggregate current flow between the counter electrode and each of the electrodes 92 and 94, is transmitted to an operational amplifier 120 where it is subtracted from the output of the amplifier 110 to obtain an output that is representative of the diffusion current flow from the electrode 90. Output from the operational amplifier 120 is likewise transmitted to an operational amplifier 122 where it is subtracted from the output of the amplifier 108 to obtain an output representative of the diffusion current flow from the electrode 88 which is biased at the highest potential.

By way of example to illustrate the operation of the multi-electrode sensor, the electrodes 88, 90, 92 and 94 are biased to nominal potentials of -1400 mV, -500 mV, -600 mV and -200 mV respectively for the simultaneous determination of NO (-1400 mV), CO_2 (-600 mV) and O_2 (-500 mV) and to compensate for residual current (-200 mV). If the outputs of the circuits for the electrodes 88, 90, 92 and 94 are identified as A, B, C and D respectively then the output from the electrode 92 equals C + D and the signal representing the diffusion current of O_2 equals (C + D) - D. Likewise the diffusion current due to CO_2 is determined

by subtracting the output from the circuit of the electrode 92 (C + D) from the output of the circuit of the electrode 90 (B + C + D). In the same fashion the diffusion current due to the electrochemical reaction of NO at the electrode 88 is determined. Circuitry of conventional design (not shown) is provided to record the outputs of the electrodes and to calculate the partial pressure of the sought after gases.

Although various embodiments and modifications have been described in the foregoing description and illustrated in the drawings, it will be understood that minor changes may be made in the details of construction as well as in the combination and arrangement of parts without departing from the spirit and scope of the invention as claimed.

What is claimed is:

1. Apparatus for electrochemically detecting a particular gas in a fluid sample, said apparatus comprising:

a body defining a reservoir for an electrolyte;

an electrically conductive sensing electrode having a working surface adjacent said permeable wall portion,

an electrically conductive counter electrode located in said body,

an electrically conductive compensating electrode located in said body adjacent said working electrode, said compensating electrode being biased to different potential than said working electrode and being exposed to said gas being tested,

circuit means for imposing a first potential between said working electrode and said counter electrode and a second potential between said compensating electrode and said counter electrode,

means for measuring current flow between said sensing electrode and said counter electrode and between said compensating and said counter electrode and for subtracting compensating electrode current from said sensing electrode current.

2. The apparatus of claim 1 wherein said compensating electrode defines a working surface disposed proximately to and in substantially the same plane as said working surface of said sensing electrode.

3. The apparatus of claim 1 wherein said compensating electrode defines a working surface disposed proximately and inwardly in said reservoir with respect to said working surface of said sensing electrode.

4. The apparatus of claim 2 wherein said compensating electrode is concentrically disposed with respect to said sensing electrode.

5. The apparatus of claim 1 wherein said compensating electrode is biased to a potential below that required for a Faradaic electrochemical reaction of the sought for substance and said sensing electrode is biased to a potential to cause a Faradaic electrochemical reaction of the sought for substance at said sensing electrode whereby the difference in current flow between said counter electrode and said sensing electrode and between said counter electrode and said compensating electrode is proportional to the partial pressure of the gas being tested for.

6. The apparatus of claim 1 wherein said sought for substance is oxygen and said sensing electrode and said compensating electrode are biased to a potential to cause a Faradaic electrochemical reaction of oxygen, the potential of said sensing electrode being greater than that of said compensating electrode and current flow between said sensing electrode and said counter electrode is measured to determine the partial pressure of oxygen in the fluid sample and said compensating electrode reduces at least a portion of dissolved oxygen in said electrolyte in the area of said sensing electrode.

7. The apparatus of claim 5 wherein said compensating electrode has an effective area at least as great as said working surface of said sensing electrode.

8. Apparatus for electrochemically detecting at least two different gases in a fluid sample comprising:

a body including an electrolyte, a wall portion of the body being permeable to the gases being tested and substantially impermeable to said electrolyte;

an electrically conductive sensing electrode having a working surface adjacent said permeable wall portion;

an electrically conductive counter electrode located in said body;

at least one electrically conductive compensating electrode located in said body adjacent said working electrode and said permeable wall portion, each said compensating electrode being biased to different potential than said working electrode and exposed to said gases being tested;

circuit means for imposing a first potential between said working electrode and said counter electrode and a different potential between each said compensating electrode and said counter electrode;

means for measuring current flow between said sensing electrode and said counter electrode and between said compensating electrode and said counter electrode and for determining the diffusion current flow between said sensing electrode and said counter electrode.

9. A method for the determination of an electrochemically reactive substance in a fluid stream comprising the steps of:

biasing a first electrode to a first potential with respect to a counter electrode, said first potential being at least at a level to cause residual current flow between said counter electrode and said first electrode;

biasing at least a second electrode to a second potential with respect to said counter electrode, said second potential being greater than said first potential;

contacting at least said second electrode with a sample from said fluid stream;

determining the signal output of said first electrode and said second electrode;

subtracting said signal output of said first electrode from said signal output of said second electrode thereby to obtain the component of said signal output of said second electrode which represents the diffusion current flow of substances in contact with said second electrode that are electrochemically active at said second potential.

10. The method of claim 8 wherein said first and said second electrodes are biased sequentially to higher first and second potentials to determine a plurality of different electrochemically reactive substances in said fluid sample.

11. The method of claim 8 wherein said first and said second electrodes are biased sequentially to lower first and second potentials to determine a plurality of different electrochemically reactive substances.

12. The method of claim 8 wherein said second potential is equivalent to the nominal concentration polarization potential of an electrochemically reactive substance being determined.

13. The method of claim 10 wherein said second potential is the equivalent of the concentration polarization potential of oxygen and oxygen is the electrochemically reactive substance being determined and thereafter said second electrode is sequentially biased to the nominal concentration polarization potential of carbon dioxide and said first electrode is biased to a potential in the concentration polarization potential range of oxygen and below that of said second electrode whereby carbon dioxide is electrochemically determined.

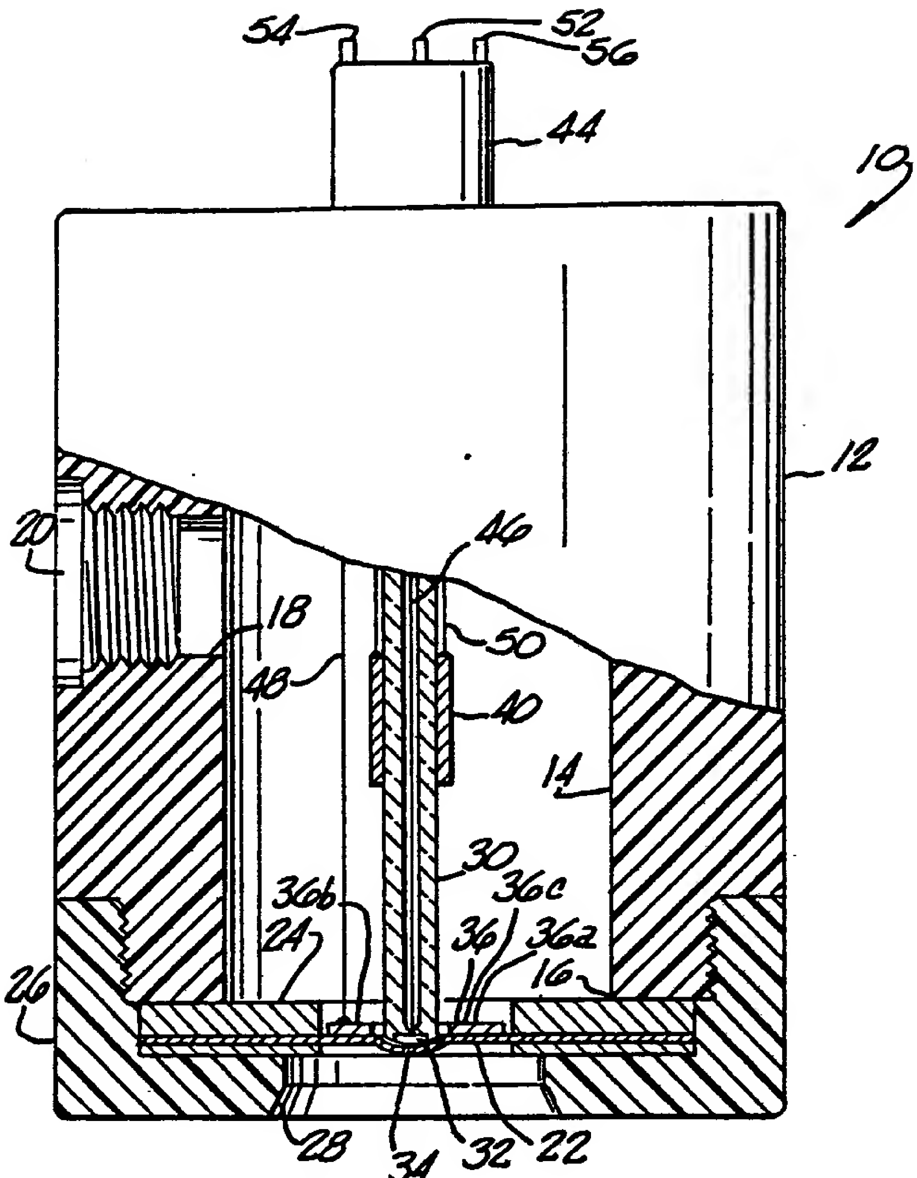
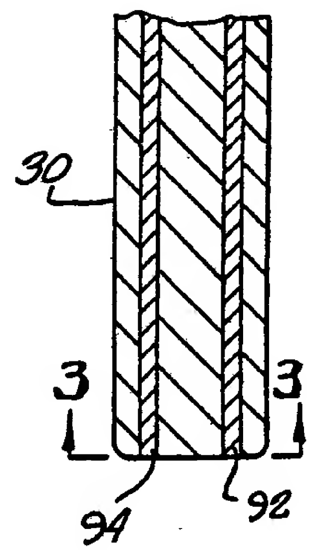


FIG. 1.

FIG. 2



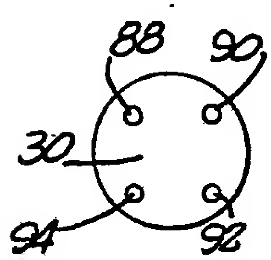
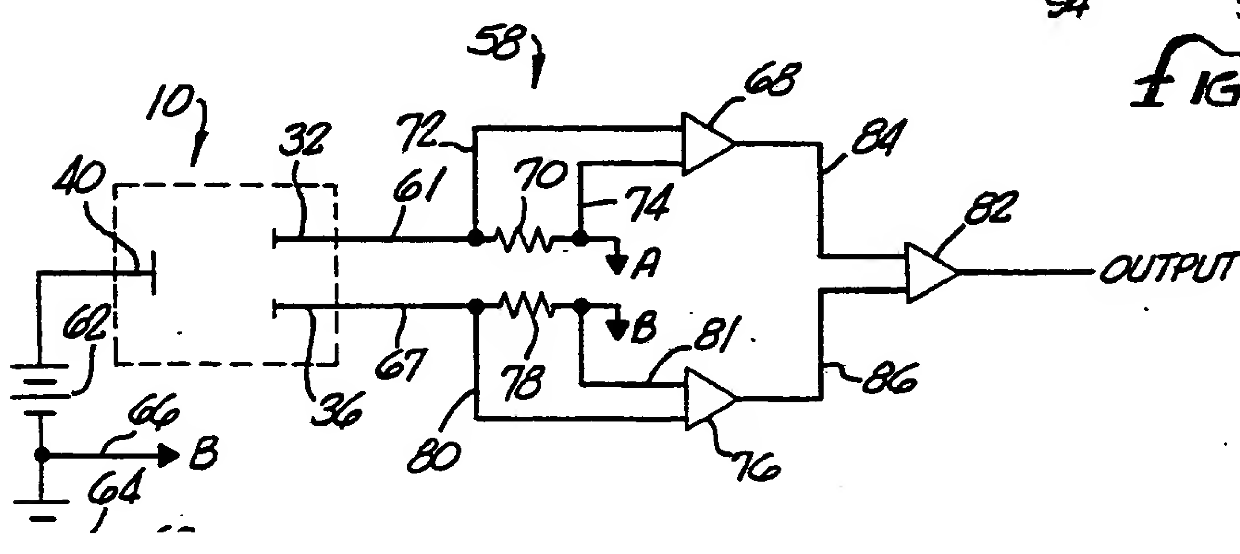


FIG. 3.



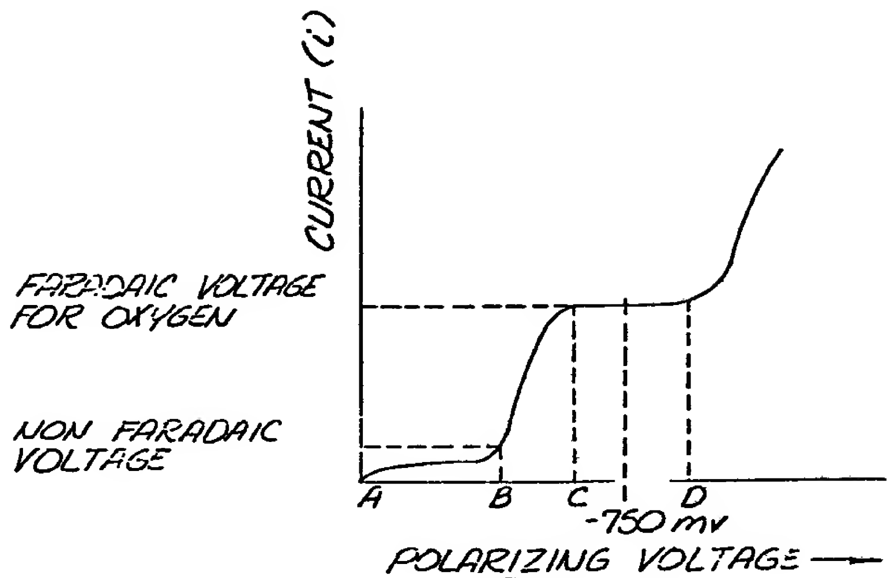

CURRENT (i)
FARADAIC VOLTAGE FOR OXYGEN
NON FARADAIC VOLTAGE
A
B
C
-750 mv
D
POLARIZING VOLTAGE

FIG. 5.

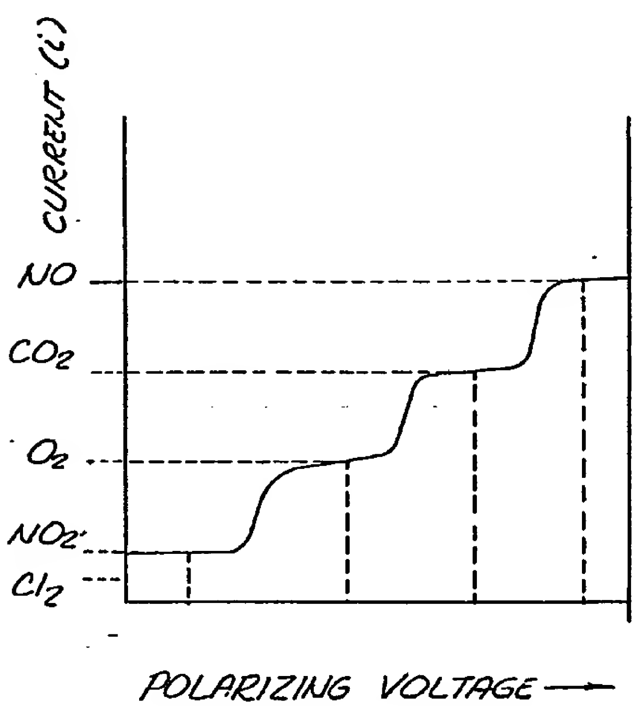

CURRENT (i)
NO
CO_2
O_2
NO_2
Cl_2
POLARIZING VOLTAGE

FIG. 6.

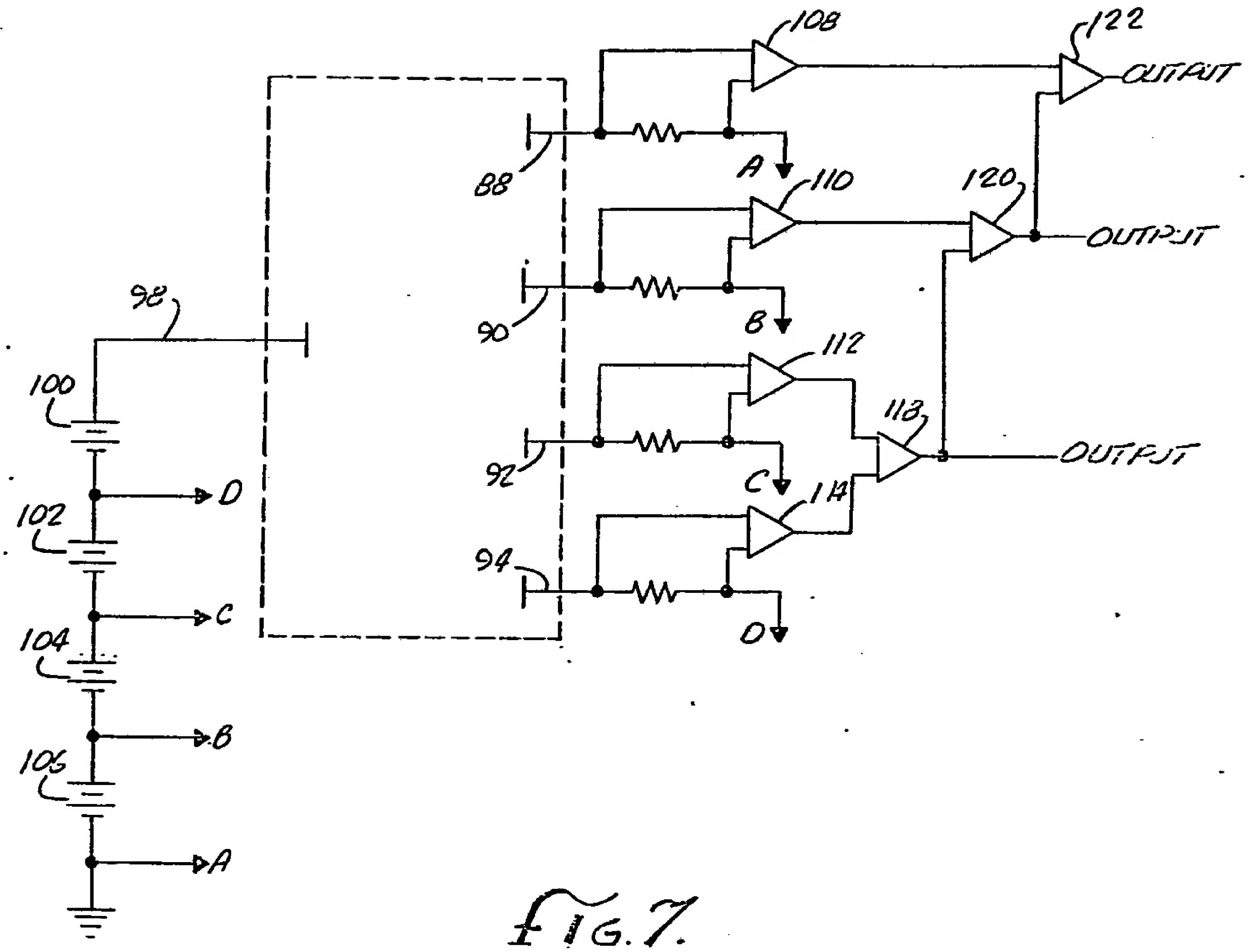

108
122
OUTPUT
88
A
110
120
OUTPUT
98
90
B
112
100
118
OUTPUT
92
C
D
114
102
94
C
D
104
B
106
A

FIG. 7.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US88/02934

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL.[4] G01N 27/46
U.S. CL. 204/1T

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
US	204/1T, 412, 415

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
Y	US, A, Re 31,916, (Oswin et al), 18 June 1985, see columns 13 and 14.	1-13
A	US, A, 3,208,926, (Eckfeldt), 28 September 1965, see figure 6.	1-13
Y	US, A, 3,413,199, (Morrow), 26 November 1968, see figure 1.	1-13
Y	US, A, 3,855,096, (Bergman), 17 December 1974, see figure 1.	1-13
Y	US, A, 4,152,233, (Chand), 01 May 1979, see column 3, line 57 to column 4, line 39.	1-13
X Y	US, A, 4,377,446, (Albery), 22 March 1983, see column 2, line 65 to column 3, line 9.	1-13 1-13

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
06 January 1989	
International Searching Authority	**Signature of Authorized Officer**
ISA/US	T. Tung

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category*	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
Y	US, A, 4,576,705, (Kondo et al), 18 March 1986, see column 2, lines 15-38.	1-13
X / Y	US, A, 4,587,003 (Tantram et al), 06 May 1986, see figure 7 and column 7, lines 21-32.	1-13 / 1-13
P,Y	US, A, 4,707,242, (Schneider et al), 17 November 1987, see column 2, lines 20-34.	1-13